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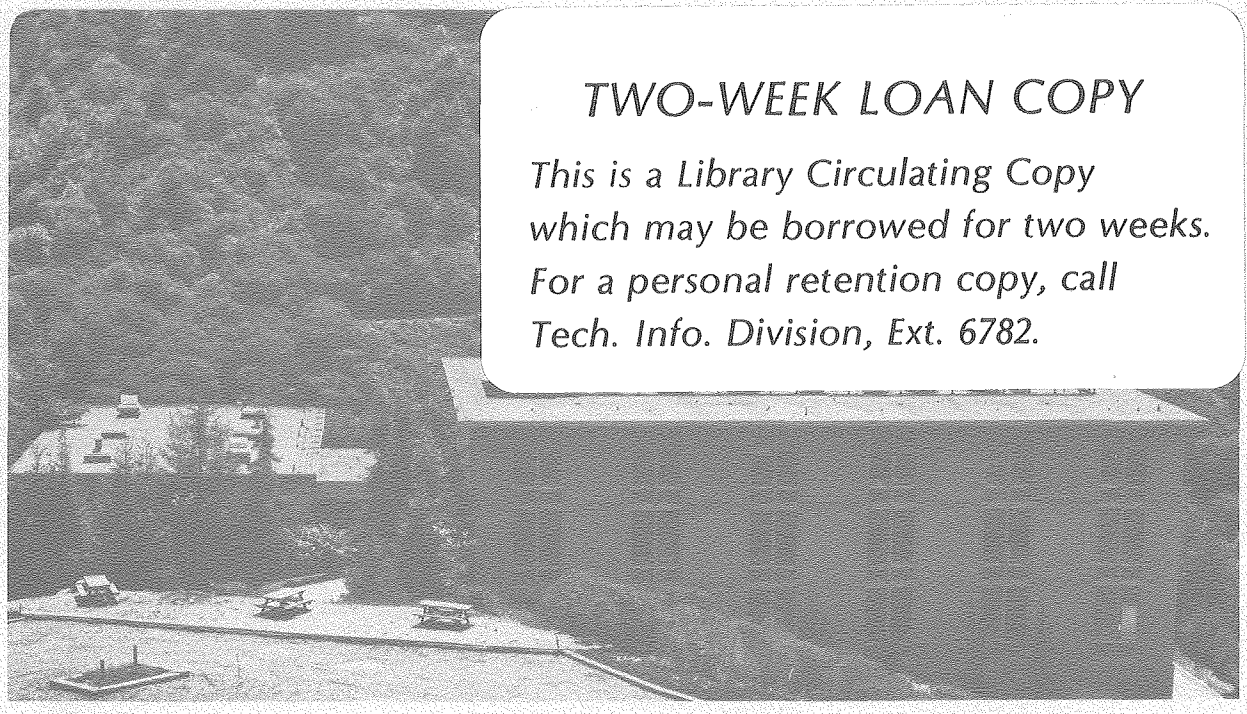

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THE PHOTOCATALYZED PRODUCTION OF HYDROGEN FROM WATER ON Pt-FREE $SrTiO_3$ SINGLE CRYSTALS IN THE PRESENCE OF ALKALI HYDROXIDES

by

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ABSTRACT

Photocatalytic hydrogen production has been observed on the illuminated surface of platinum-free $SrTiO_3$ crystals immersed in alkaline aqueous solutions or covered by water vapor saturated films of NaOH. The rate of hydrogen production increases with the concentration of the NaOH solution surrounding the crystal.

Semiconductor surfaces can serve as photosensitizers for small molecules which do not of themselves absorb solar photons. One application of such sensitizers is the photoassisted decomposition of water to hydrogen and oxygen. Most previous work on this process has concentrated on photoelectrochemical cells employing oxide semiconductor photoanodes for oxygen evolution and platinum cathodes for the evolution of hydrogen. We report here the sustained photogeneration of hydrogen on $SrTiO_3$ single crystal surfaces by a different mechanism, when no platinum coating or platinum counterelectrode is present. Hydrogen yields far exceed the monolayer amounts ($\sim 10^{15}$ molecules/cm^2) to be expected from a surface stoichiometric reaction. The reaction takes place upon illumination of the crystal with bandgap radiation ($h\nu \geq 3.2$eV) in aqueous alkaline solution. The rate of hydrogen evolution increased with increasing hydroxide concentration in the solution. We also report the use of water vapor as a reactant through saturation of a layer of a basic deliquescent compound, such as NaOH, which coated the crystal. The photocatalytic generation of hydrogen on the illuminated surface of metal-free $SrTiO_3$ crystals shows that strongly reductive as well as oxidative reactions can be carried out and sustained on illuminated oxide semiconductors. It appears that a wide range of photocatalytic reactions may be carried out under conditions not amenable to the operation of photoelectrochemical cells by taking advantage of this new mechanism.

Single crystal wafers of $SrTiO_3$ cut within 1° of the (111) plane were dipped in a saturated NaOH solution, dried to leave $\sim 30\mu$ of NaOH on the surfaces, and inserted into a stainless steel vacuum cell equipped with a sapphire window. The crystal was held in a quartz glass basket; no metal was in contact with it or

the NaOH layer. The cell was evacuated and then backfilled with a saturation pressure of water vapor (∿20 torr). A stainless steel bellows pump circulated the vapor and product gases around a closed loop which included a gas sampling valve. A gas chromatograph equipped with a thermal conductivity detector and a molecular sieve 5A column and operated with an argon carrier gas allowed the hydrogen concentration in the loop to be periodically measured. The crystal was illuminated with the focussed, water-filtered output of a 500W high pressure mercury lamp which provided a flux of bandgap ($h\nu \geq 3.2$ eV) photons of $\sim 10^{16} cm^{-2} sec^{-1}$. The use of colored glass filters allowed the separation of bandgap and sub-bandgap ($h\nu < 3.2$ eV) radiation.

Metal-free crystals coated with NaOH and illuminated in water vapor yielded hydrogen at rates of 20-100 monolayers (1 monolayer $\equiv 1 \times 10^{15}$ molecules/cm^2 illuminated surface) per hour. This range of rates was obtained on both stoichiometric (insulating) and prereduced (n-type) crystals. No hydrogen production was obtained when any of the following were absent: bandgap light, saturation pressure of water vapor, $SrTiO_3$, or a coating of a basic deliquescent compound such as NaOH, Cs_2CO_3, or KOH greater than 2μ thick. Similar results were obtained when metal-free crystals were immersed in 10 ml of thoroughly outgased aqueous solution in a pyrex vacuum cell and then illuminated. (Fig.1). Metal-free crystals yielded up to 50 monolayers/hr of hydrogen when illuminated in 20N NaOH at 41°C. This rate could be maintained for tens of hours. Hydrogen production was observed only in basic solutions, and the rate of hydrogen photogeneration increased with the concentration of NaOH solutions, as shown in Figure 2. Sealing off the non-illuminated surfaces of a metal-free $SrTiO_3$ crystal with ultrahigh vacuum compatible epoxy caused no decrease in the rate of

hydrogen photogeneration, indicating that hydrogen was produced on the illuminated surface. The epoxy was shown not to be a source of hydrogen.

For comparison, experiments were also performed with platinized crystals. The backs of such crystals were coated with platinum through the thermal reduction of chloroplatinic acid. Platinized, prereduced crystals yielded hydrogen at rates up to 1600 monolayers/hr when coated with NaOH and illuminated in water vapor. Rates up to 4500 monolayers/hr were observed in 20N NaOH electrolyte. Hydrogen photogeneration on platinized crystals showed a hydrogen concentration dependence similar to that observed on metal-free crystals. Covering the platinized surfaces with epoxy decreased the hydrogen evolution rates to those observed on metal-free crystals. A standard $SrTiO_3$/Pt photoelectrochemical cell[2] with discrete electrodes was also operated in the vacuum cell and gave hydrogen generation rates about five times those observed on platinized crystals, probably due to the provision of a true ohmic contact between the $SrTiO_3$ and platinum by use of a Ga-In eutectic.

In photoelectrochemical cells or platinized crystals of n-type semiconductors, photogenerated electrons and holes are separated by the electric field within the semiconductor depletion layer. Holes rise to the semiconductor surface where they can oxidize solution species. Electrons are driven into the semiconductor bulk and then to the platinum surfaces where reductive chemistry occurs. Hydrogen production on metal-free crystals occurs at the illuminated semiconductor surface, presumably through the generation of local reduced and oxidized centers and the crystal surface. Photoemission studies of $SrTiO_3$(111) surfaces in our laboratory[4] have shown that a reduced Ti^{3+} surface species can be regenerated by shining bandgap light upon the oxygen-covered surface. The regeneration of Ti^{3+} is accompanied by oxygen photodesorption.

Such reduced centers may be involved in the photocatalytic hydrogen production reported here.

High hydroxide concentrations were required for hydrogen production from metal-free crystals and also greatly increased the rates obtained on platinized crystals. Hydroxide ions at or near the surface may serve as facile hole acceptors, decreasing the probability of electron hole recombination and increasing the mean lifetime of electrons at the surface. Hydroxyl groups can be monitored on $SrTiO_3(111)$ surfaces by photoelectron spectroscopy[4] and their effects on the photochemistry are being further investigated.

Acknowledgement

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Figure Captions

Figure 1. Hydrogen photogeneration on a metal-free stoichiometric $SrTiO_3$ crystal upon illumination in 20N aqueous NaOH at 44°C.

Figure 2. Hydrogen photoproduction on a metal-free stoichiometric $SrTiO_3$(111) crystal as a function of aqueous NaOH concentration at 44°C.

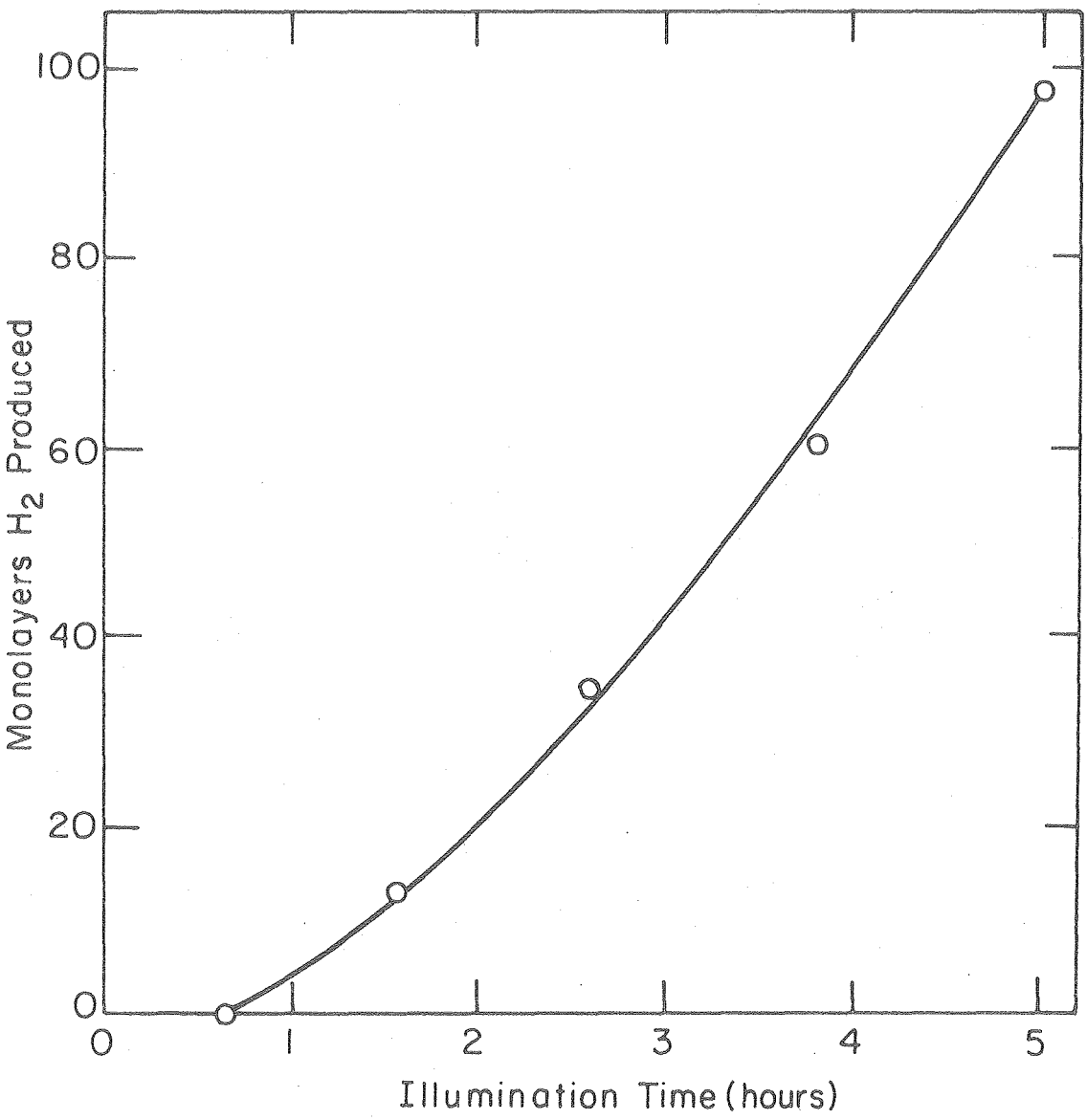
100
80
60
40
20
0
Monolayers H_2 Produced
0
1
2
3
4
5
Illumination Time (hours)
XBL 801 4602

Fig.1

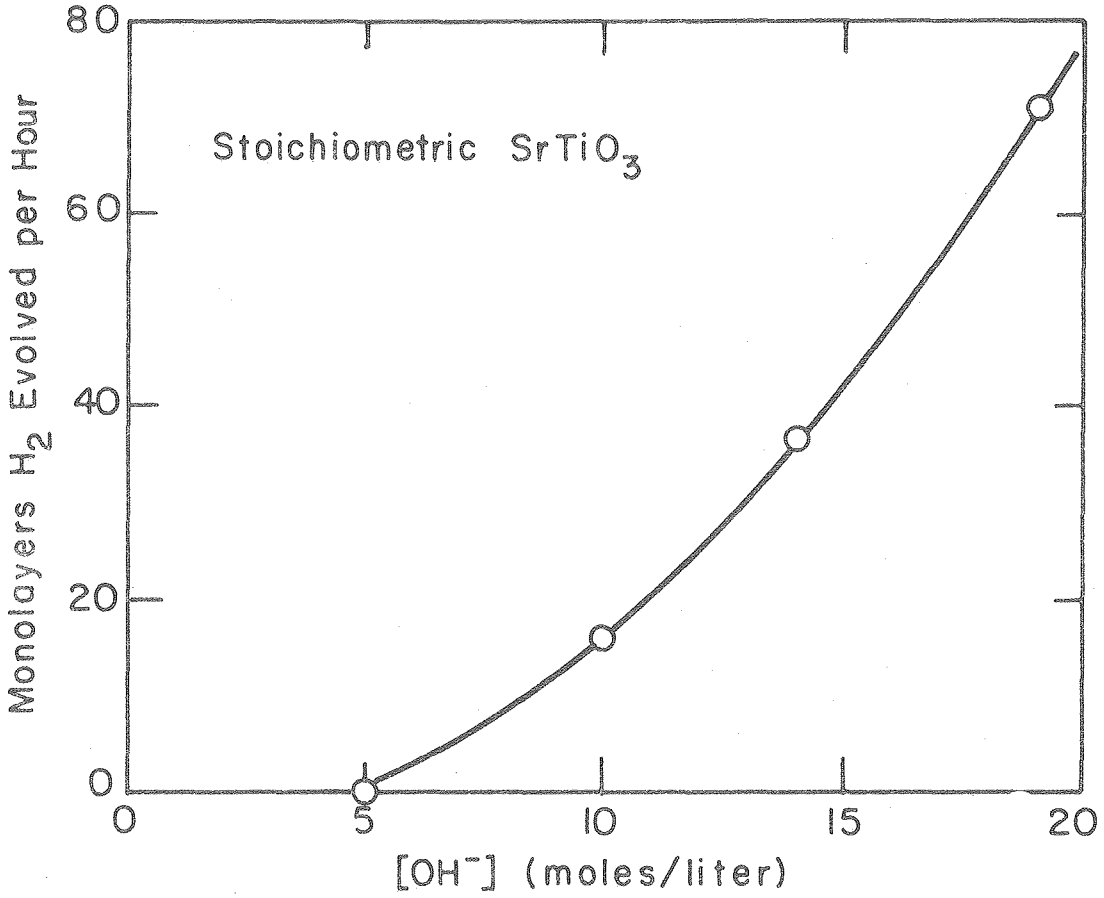

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Fig.2